



Preparation of functionalized graphene by simultaneous reduction and surface modification and its polymethyl methacrylate composites through latex technology and melt blending

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HIGHLIGHTS

- A novel way reduces GO to graphene and simultaneously functionalizes the graphene.
- PMMA/graphene composites are prepared by latex technology and melt mixing.
- Strong covalent bonds are formed between graphene sheets and PMMA matrix.
- The PMMA/graphene composites exhibit exfoliated morphology and good dispersion.
- The PMMA/graphene composites possess enhanced mechanical and thermal properties.

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ABSTRACT

Graphene is a kind of very promising filler for polymer composites, but its irreversible aggregation when introduced into polymers is a challenge for property enhancements and limits its industrial application. To address this, we report one-step covalent functionalization and simultaneous reduction of graphite oxide (GO) with hydroxyethyl acrylate (HEA), resulting in a functionalized graphene with double bonds. The functionalized graphene obtained, noted as FGN, is successfully incorporated into polymethyl methacrylate (PMMA) matrix by latex technology and melt blending. Latex technology is used for the pretreatment of FGN through emulsion copolymerization between methyl methacrylate (MMA) monomers and FGN double bonds. After pretreatment of FGN, covalent attachment of PMMA particles to the edges of FGN sheets can effectively prevent their agglomeration and markedly improve their dispersion in the polymer matrix. Since these PMMA particles act as good compatibilizers in the interface between FGN and PMMA matrix during the melt mixing process, the PMMA/FGN composites obtained exhibit exfoliated morphology and very good dispersion, as evinced by the results from X-ray diffraction (XRD) and transmission electron microscopy (TEM). When even a small amount of FGN (≤ 1.0 wt%) is incorporated, the thermal properties and mechanical properties of PMMA/FGN composites are enhanced significantly. The glass transition temperature (T_g) increases from 103.8 to 110.5 °C, while the tensile strength increases by 31.0% (1.0 wt% FGN addition). Moreover, the storage modulus of PMMA/FGN composites increases by 27% (1.0 wt% FGN addition) at room temperature. These enhancements are attributed to the strong chemical interaction between the FGN sheets and PMMA and the good distribution of FGN sheets in the PMMA matrix.

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1. Introduction

Graphene, an atomically thin sheet composed of two-dimensional π -conjugated sp^2 carbons, has attracted increasing

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attention in recent years owing to its outstanding mechanical, thermal, and electrical properties, as well as a large surface area [1–4]. Polymer/graphene composites, as an important application of graphene, are very promising due to the significant improvements in mechanical, thermal, flame retardancy and electrical properties achieved by the addition of very small amounts of graphene [5]. Kotov et al. reported graphene as being the most suitable filler, better than carbon nanotubes and other conventional nanofillers

[6]. To date, various techniques have been developed for producing graphene, including micromechanical cleavage, chemical vapor deposition and liquid-phase exfoliation of graphite and reduction of GO by chemical reducing agents and thermal treatment. The reduction of GO, which can mass produce graphene, is suitable for polymer/graphene composites [7–9]. However, the graphene obtained by chemical reduction of GO always re-aggregate when it is introduced into polymers, due to the intrinsic van der Waals force between graphene layers [10,11].

Three methods are used to disperse graphene into polymers at present: in situ polymerization, solvent blending and melt blending. In situ polymerization and solvent blending usually result in good dispersion while the melt blending causes poor dispersion [12]. Kim et al. prepared polyurethane/graphene and polyethylene/graphene composites via solvent blending, in situ polymerization or melt blending. Melt blending resulted in much poorer dispersion than solvent blending and in situ polymerization [13,14]. In the available literature, very few polymer/graphene composites are prepared using melt blending: most papers focus on in situ polymerization or solvent blending. However, the greatest drawback of in situ polymerization and solvent blending is that large amounts of organic solvent, which is poisonous and not convenient for industrial processing, are required [12,15]. The melt blending approach, economical, ease to process and apply practically, has been widely used in the plastic industry. Given these advantages, the dispersion challenge of melt blending should be overcome, as this method remains the most promising industrial application of graphene.

Latex technology, as an ideal alternative method, has been widely used to prepare polymer/carbon nanotube (CNT) composites by mixing polymer latex with a CNT aqueous dispersion [16–20]. Using this technology, nanofiller particles are wrapped by polymer latex particles, and form a segregated network. Latex technology has recently been applied to prepare polymer/graphene composites with various kinds of polymers, such as polyethylene, polypropylene, polystyrene, polycarbonate, and poly(styrene-co-acrylonitrile) [21–25]. The polymer/graphene composites prepared using latex technology exhibited better dispersion and enhanced properties compared with the polymer/graphene composites prepared by solution blending [23]. However, the physical adsorption between polymer latex and nanofillers is not strong enough to prevent the deposition of some nanofiller particles in the polymer latex solution, leading to the poor distribution of nanofillers in the polymer matrix. As is well known, strong interaction between the polymer matrix and the graphene layers is beneficial to dispersion [26]. Thus, strengthening the chemical interaction between polymer chains and graphene is a feasible approach to improve dispersion.

In the present work, we report a convenient method to reduce GO to graphene and simultaneously functionalize the graphene. Before melt mixing with PMMA, the functionalized graphene, FGN, was pretreated via emulsion polymerization of MMA, unlike in earlier research, which employed either simple emulsion polymerization or melt blending, but never in combination [27–30]. Both latex technology and melt blending methods were used together in our case to prepare the PMMA/FGN composites. The FGN sheets were successfully wrapped by PMMA particles using latex technology. The PMMA particles on the FGN sheets were linked to the FGN surface with strong covalent bonds. It is found that PMMA particles not only prevent the re-stacking of the final graphene sheets, but also act as good compatibilizers between FGN sheets and PMMA matrix during the melt blending process, resulting in good dispersion of FGN in PMMA matrix. Due to the improved dispersion of FGN and the strong interaction between FGN and PMMA matrix, the PMMA/FGN composites exhibit greater improvement in thermal properties and mechanical properties

than the composites obtained via the melt blending alone. This research provides a new direction to the production of polymer/graphene composites, such as polystyrene, polyacrylonitrile, poly(vinyl chloride), and poly vinyl acetate, which can all be prepared by free radical emulsion polymerization.

2. Experimental section

2.1. Raw materials

Natural flake graphite (EG) with an average particle size of 325 mesh and a purity of >99% was supplied by Qingdao Tianhe Graphite Co., Ltd. (China). Potassium permanganate (KMnO_4), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3), hydrogen peroxide (H_2O_2 , 30% aq.), tetrahydrofuran (THF), thionylchloride (SOCl_2), N,N-dimethylformamide (DMF), triethylamine (TEA), HEA, MMA, potassium peroxydisulfate (KPS), sodium lauryl sulfate (SDS) and sodium chloride (NaCl) were of analytical grade and provided by Sinopharm Chemical Reagent Co., Ltd. PMMA (CM211) was obtained from CHI MEI Co., Ltd. (Taiwan). THF was refluxed with sodium, and then distilled before use. MMA was used after further purification including retarder removal, water removal and reduced pressure distillation. $\text{K}_2\text{S}_2\text{O}_8$ was further purified by recrystallization from methanol. TEA, HEA, DMF and SOCl_2 were purified by reduced pressure distillation before use. All other chemicals were used as received.

2.2. Preparation of GO and FGN

GO was prepared by a modified Hummers' method from flake graphite. First, flake graphite (6.0 g), H_2SO_4 (200 mL) and NaNO_3 (6.0 g) were placed in a four-neck flask and fully cooled to 3–4 °C in an ice bath. After 15 min mechanical stirring, KMnO_4 (25 g) was slowly added over 10 min. The mixture was further stirred for 1 h at 8–10 °C and then heated to 35 °C. The temperature was accurately maintained at 34–36 °C for 2 h. After that, 200 mL H_2O was dripped into the mixture while the temperature of the reactants was kept at 96–100 °C for 30 min. The obtained viscous mud was diluted in 800 mL water, and then H_2O_2 was added to reduce the un-reacted oxidant until the slurry turned golden yellow. Wet GO was finally obtained after centrifugation and washing with dilute HCl and hot deionized water.

The preparation of FGN is presented in Scheme 1. First, GO (2.5 g) was treated with SOCl_2 (100 mL) under ultrasonic treatment for 5 h, and then refluxed in the presence of DMF (1.5 mL) at 70 °C for 24 h under nitrogen protection. After evaporation of volatile fractions under reduced pressure, fresh distilled THF (150 mL), TEA (4.04 g, 0.04 mol) and HEA (4.64 g, 0.04 mol) were added to the residue. The reaction mixture was stirred vigorously at room temperature overnight and then filtered over a 0.22 μm PTFE membrane. The filter cake was washed with deionized water several times and dried in a vacuum desiccator at room temperature, affording a black solid product. During the process, GO was reduced into graphene and the obtained novel graphene was functionalized by double bond.

2.3. Preparation of PMMA/FGN composites

The PMMA/FGN composites were prepared using two different methods. The first method comprised two steps, as described in Scheme 2. Step 1 (Scheme 2a) was the pretreatment of FGN via emulsion polymerization. First, FGN (1.0 g) was ultrasonically dispersed in 50 mL water for 1 h. In a 250 mL glass reactor equipped with a reflux condenser, stainless-steel stirrer and thermometer, SDS (1.2 g) was dissolved in 70 mL distilled water, to which the

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